

Time reversibility and nonequilibrium thermodynamics of second-order stochastic systems with inertia

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We rigorously investigate the condition of time reversibility as well as detailed balancing for the second-order stochastic process with inertia. We show that the time-reversibility could not even guarantee the steady state to be at thermal equilibrium. The real thermal equilibrium demands the other condition of detailed balance regarding the interaction between the internal system and its contacting reservoir, i.e. agreeing with the Maxwell-Boltzmann velocity distribution. We show that frictional force naturally emerges as the only odd term of the force at thermal equilibrium when both conditions of detailed balance are satisfied. The two conditions correspond to two different previously reported entropy production rates respectively, followed by two equations of entropy balance. When the external force is only dependent on the spatial coordinates, the two entropy balance equations become the same. The entropy production rates of the second-order stochastic process and its corresponding overdamped first-order process without inertia are only consistent if there is no temperature gradient. In the presence of temperature gradient, we prove that the former must be at nonequilibrium (time-irreversible), while the latter could still possibly be time-reversible.

The principle of microscopic reversibility in thermodynamics states that the dynamic process of equilibrium ensembles is invariant with respect to the inversion in time [1]. The meaning of such a time-reversibility is two folds: the forward trajectory $X(t)$ and its time-reversed one $X(-t)$ are both the solutions of a same deterministic microscopic equations of motion, or the statistical descriptions of the forward and backward processes are exactly the same. In statistical mechanics, it is formulated in the second sense, and the principle of detailed balance and the Onsager reciprocal relations are both consequences of microscopic reversibility [1–3].

It is generally believed that time-reversibility of the statistical description for the process, or the detailed balance, is equivalent to the thermal equilibrium, which has already been proved for chemical kinetics as well as overdamped Scholuchowski equations [1, 4–9]. Also, the principle of microscopic reversibility for linear systems containing odd functions of velocities has been formulated by Casimir [10] and developed by Onsager and Machlup [11] half an century ago. These odd functions arise from the inertia of the system, which could be expressed as the time-derivatives of other even functions.

Time-reversibility of second-order stochastic systems with inertia — In order to investigate the time-reversibility and its relation to thermal equilibrium for such a second-order system, we consider a general model describing the dynamics of single particle in the phase space

$$m \frac{d^2 \mathbf{X}}{dt^2} = \mathbf{F}(\mathbf{X}, \dot{\mathbf{X}}) + \xi(t), \quad (1)$$

which could be rewritten as the Langevin equation

$$\begin{aligned} \frac{d\mathbf{X}}{dt} &= \mathbf{V}; \\ m \frac{d\mathbf{V}}{dt} &= \mathbf{F}(\mathbf{X}, \mathbf{V}) + \xi(t), \end{aligned} \quad (2)$$

where $\xi(t)$ represents Gaussian white noise with intensity D and m is the mass. It is also known as the Kramers' equation when $\mathbf{F}(\mathbf{X}, \mathbf{V}) = -\eta\mathbf{V} - \nabla_{\mathbf{X}}U(\mathbf{X})$, in which $\eta = \frac{D}{2k_B T}$ is the frictional coefficient and $U(\mathbf{X})$ is a potential [12].

Hence the time-reversibility of such a stochastic system, is formulated as

$$\begin{aligned} \mathbb{P}(\mathbf{X}(0) = \mathbf{x}_1, \mathbf{V}(0) = \mathbf{v}_1, \mathbf{X}(t) = \mathbf{x}_2, \mathbf{V}(t) = \mathbf{v}_2) \\ = \mathbb{P}(\mathbf{X}(0) = \mathbf{x}_2, \mathbf{V}(0) = -\mathbf{v}_2, \mathbf{X}(t) = \mathbf{x}_1, \mathbf{V}(t) = -\mathbf{v}_1), \end{aligned}$$

for any coordinates $\mathbf{x}_1, \mathbf{x}_2$, velocities $\mathbf{v}_1, \mathbf{v}_2$ and time t .

It follows that

$$\begin{aligned} \rho_0(\mathbf{x}_1, \mathbf{v}_1) p_t(\mathbf{x}_2, \mathbf{v}_2 | \mathbf{x}_1, \mathbf{v}_1) \\ = \rho_0(\mathbf{x}_2, -\mathbf{v}_2) p_t(\mathbf{x}_1, -\mathbf{v}_1 | \mathbf{x}_2, -\mathbf{v}_2), \end{aligned} \quad (3)$$

where $\rho_0(\mathbf{x}, \mathbf{v}) = \mathbb{P}(\mathbf{X}(0) = \mathbf{x}, \mathbf{V}(0) = \mathbf{v})$ is the initial distribution and

$$\begin{aligned} p_t(\mathbf{x}, \mathbf{v} | \tilde{\mathbf{x}}, \tilde{\mathbf{v}}) \\ = \mathbb{P}(\mathbf{X}(t) = \mathbf{x}, \mathbf{V}(t) = \mathbf{v} | \mathbf{X}(0) = \tilde{\mathbf{x}}, \mathbf{V}(0) = \tilde{\mathbf{v}}) \end{aligned}$$

is the transition probability density function. The condition of microscopic reversibility formulated in connection to transition probabilities is firstly discovered by Tolman [2].

The time evolution of the function $p_t(\mathbf{x}, \mathbf{v} | \tilde{\mathbf{x}}, \tilde{\mathbf{v}})$ obeys

both the Kolmogorov forward and backward equations:

$$\begin{aligned} \frac{dp_t(\tilde{\mathbf{x}}, \tilde{\mathbf{v}}|\mathbf{x}, \mathbf{v})}{dt} &= -\nabla_{\tilde{\mathbf{x}}} \cdot (\tilde{\mathbf{v}}p_t) - \nabla_{\tilde{\mathbf{v}}} \cdot \left(\frac{\mathbf{F}(\tilde{\mathbf{x}}, \tilde{\mathbf{v}})}{m} p_t \right) \\ &\quad + \frac{D}{2m^2} \nabla_{\tilde{\mathbf{v}}} \cdot \nabla_{\tilde{\mathbf{v}}} p_t, \end{aligned} \quad (4)$$

$$\begin{aligned} \frac{dp_t(\tilde{\mathbf{x}}, \tilde{\mathbf{v}}|\mathbf{x}, \mathbf{v})}{dt} &= \mathbf{v} \cdot \nabla_{\mathbf{x}} p_t + \frac{\mathbf{F}(\mathbf{x}, \mathbf{v})}{m} \cdot \nabla_{\mathbf{v}} p_t \\ &\quad + \frac{D}{2m^2} \nabla_{\mathbf{v}} \cdot \nabla_{\mathbf{v}} p_t. \end{aligned} \quad (5)$$

Then we can apply these forward and backward equations to derive the condition for time-reversibility. The time evolution of

$$f_t(\mathbf{x}_2, \mathbf{v}_2, \mathbf{x}_1, \mathbf{v}_1) = \frac{\rho_0(\mathbf{x}_2, -\mathbf{v}_2)}{\rho_0(\mathbf{x}_1, \mathbf{v}_1)} p_t(\mathbf{x}_1, -\mathbf{v}_1 | \mathbf{x}_2, -\mathbf{v}_2)$$

could be derived from the backward equation (5), i.e.

$$\begin{aligned} \frac{df_t}{dt} &= -\nabla_{\mathbf{x}_2} \cdot (\mathbf{v}_2 f_t) - \nabla_{\mathbf{v}_2} \cdot \left(\frac{\mathbf{F}^{rev}}{m} f_t \right) \\ &\quad + \frac{D}{2m^2} \nabla_{\mathbf{v}_2} \cdot \nabla_{\mathbf{v}_2} f_t + \mathbf{S} \cdot f_t, \end{aligned}$$

where

$$\mathbf{F}^{rev}(\mathbf{x}_2, \mathbf{v}_2) = \mathbf{F}(\mathbf{x}_2, -\mathbf{v}_2) + \frac{D}{m} \nabla_{\mathbf{v}_2} \log \rho_0(\mathbf{x}_2, -\mathbf{v}_2)$$

and

$$\begin{aligned} &\mathbf{S}(\mathbf{x}_2, \mathbf{v}_2) \\ &= \left[\nabla_{\mathbf{x}_2} \cdot (\mathbf{v}_2 \rho_0(\mathbf{x}_2, -\mathbf{v}_2)) + \nabla_{\mathbf{v}_2} \cdot \left(\frac{\mathbf{F}(\mathbf{x}_2, \mathbf{v}_2)}{m} \rho_0(\mathbf{x}_2, -\mathbf{v}_2) \right) \right. \\ &\quad \left. + \frac{D}{2m^2} \nabla_{\mathbf{v}_2} \cdot \nabla_{\mathbf{v}_2} \rho_0(\mathbf{x}_2, -\mathbf{v}_2) \right] / \rho(\mathbf{x}_2, -\mathbf{v}_2). \end{aligned}$$

According to the condition (3) of time-reversibility, $f_t(\mathbf{x}_2, \mathbf{v}_2, \mathbf{x}_1, \mathbf{v}_1) = p_t(\mathbf{x}_2, \mathbf{v}_2 | \mathbf{x}_1, \mathbf{v}_1)$, which should be the fundamental solution of the Kolmogorov forward equation (4). Hence the necessary and sufficient condition for time-reversibility is

$$\begin{aligned} \mathbf{F}^{rev} &= \mathbf{F}; \\ \mathbf{S}(\mathbf{x}_2, \mathbf{v}_2) &= 0. \end{aligned} \quad (6)$$

The condition $\mathbf{S}(\mathbf{x}_2, \mathbf{v}_2) = 0$ just guarantees that the distribution $\rho_0 = \rho^{ss}$ is the unique stationary solution to the well-known Fokker-Planck equation of the probability distribution $\rho_t(\mathbf{x}, \mathbf{v})$ in the phase space

$$\frac{\partial}{\partial t} \rho_t = -\nabla_{\mathbf{x}} \cdot \mathbf{J}_{\mathbf{x}} - \nabla_{\mathbf{v}} \cdot \mathbf{J}_{\mathbf{v}}, \quad (7)$$

where the coordinate flux $\mathbf{J}_{\mathbf{x}} = \mathbf{v} \rho_t$ and the velocity flux $\mathbf{J}_{\mathbf{v}} = \frac{\mathbf{F}}{m} \rho_t - \frac{D}{2m^2} \nabla_{\mathbf{v}} \rho_t$.

Define another function $\epsilon \mathbf{F}(\mathbf{x}, \mathbf{v})$, which reverses all the odd variables including \mathbf{v} under the time reversal, then the condition (6) of time-reversibility could be

rewritten as

$$\begin{aligned} \frac{D}{m} \nabla_{\mathbf{v}} \log \rho_0 &= \mathbf{F} - \epsilon \mathbf{F}; \\ 2D \mathbf{v} \cdot \nabla_{\mathbf{x}} \log \rho_0 &= - \left[\mathbf{F}^2 - (\epsilon \mathbf{F})^2 + \frac{D}{m} \nabla_{\mathbf{v}} \cdot (\mathbf{F} + \epsilon \mathbf{F}) \right]. \end{aligned} \quad (8)$$

Furthermore, it is easy to prove that the coordinate fluxes are odd while the velocity fluxes are even with respect to all the odd variables including \mathbf{v} in the case of time-reversibility, i.e.

$$\begin{aligned} \mathbf{J}_{\mathbf{x}} &= -\epsilon \mathbf{J}_{\mathbf{x}} \\ \mathbf{J}_{\mathbf{v}} &= \epsilon \mathbf{J}_{\mathbf{v}}. \end{aligned} \quad (9)$$

Hence the total observed fluxes in the subspaces of coordinates $\int \mathbf{J}_{\mathbf{x}} d\mathbf{v}$ vanishes.

It could be regarded as the condition of detailed balance, which is quite different from that of the overdamped Langevin dynamics [7]. In steady state, the condition (9) of detailed balance is equivalent to the condition of time-reversibility (8).

Time-reversible stationary distribution and another condition of detailed balance— Interestingly, a lot of steady-state probability density ρ^{ss} could satisfy the time-reversibility condition (8) for certain force \mathbf{F} . It is because once we have a well defined density function ρ^{ss} , then we could find an odd and an even function $\mathbf{f}_1 (= -\epsilon \mathbf{f}_1)$ and $\mathbf{f}_2 (= \epsilon \mathbf{f}_2)$, which are the solution of the equations

$$\begin{aligned} \frac{D}{m} \nabla_{\mathbf{v}} \log \rho^{ss} &= \mathbf{f}_1; \\ 2m \mathbf{v} \cdot \nabla_{\mathbf{x}} \rho^{ss} &= -\nabla_{\mathbf{v}} \cdot (\mathbf{f}_2 \rho^{ss}). \end{aligned} \quad (10)$$

The even function \mathbf{f}_2 is not generally unique, since we can add any magnetic term $\mathbf{B} \times \mathbf{v}$ to \mathbf{f}_2 in which \mathbf{B} is also odd under time reversal. Then $\mathbf{F} = \frac{\mathbf{f}_1 + \mathbf{f}_2}{2}$ would make the second-order stochastic process (1) become time-reversible.

The simplest analytical example is the AFM (atomic force microscopy) experiment performed on nanodevices [14, 15], in which a linear velocity-dependent feedback control is applied. To be more precise, $\mathbf{F} = -\eta \mathbf{v} - \alpha \mathbf{v} - \nabla_{\mathbf{x}} U(\mathbf{x})$ with a positive constant α . The corresponding stationary distribution is $C \exp[-(\frac{1}{2} m \mathbf{v}^2 + U(\mathbf{x})) / k_B T_{eff}]$, in which the effective temperature $T_{eff} = \frac{\eta}{\eta + \alpha} T$.

It is easy to check that the condition (8) of time-reversibility is satisfied in its steady state, where $\frac{\mathbf{F} - \epsilon \mathbf{F}}{2} = -(\eta + \alpha) \mathbf{v}$. However, the effective temperature $T_{eff} = \frac{\eta}{\eta + \alpha} T$ is less than the temperature T of the heat reservoir, which implies that it is not in thermal equilibrium and then be released to the external agent in the form of work. Thus we realize that there is another condition of detailed balance beyond the time-reversibility of

the internal stochastic process in order to guarantee the thermal equilibrium.

When there is no external feedback of velocity in the AFM experiments, i.e. $\alpha = 0$, the stochastic process is in equilibrium with stationary distribution $\tilde{\rho}^{ss}(\mathbf{x}, \mathbf{v}) \propto \exp[-\frac{\frac{1}{2}m\mathbf{v}^2 + U(\mathbf{x})}{k_B T}]$, i.e. $T_{eff} = T$.

The thermal contact between the internal stochastic dynamics (1) with its heat reservoir is due to the collisions between the internal single particle and the large number of equilibrium-fluctuating molecules in the reservoir. Thus the principle of detailed balance for collisions tells that [16, 17]

$$\tilde{\rho}^{ss}(\mathbf{v}_1) \cdot \rho^{ss}(\mathbf{x}, \mathbf{v}_2) = \tilde{\rho}^{ss}(\mathbf{v}_1') \cdot \rho^{ss}(\mathbf{x}, \mathbf{v}_2'), \quad (11)$$

in which $\tilde{\rho}^{ss}(\mathbf{v})$ is the Maxwell velocity distribution of the reservoir, and the kinetic energy should be preserved during the collision, i.e. $m' \mathbf{v}_1^2 + m \mathbf{v}_2^2 = m' (\mathbf{v}_1')^2 + m (\mathbf{v}_2')^2$, where m' is the mass of the molecule in the reservoir.

Hence

$$\begin{aligned} \frac{\rho^{ss}(\mathbf{x}, \mathbf{v}_2)}{\rho^{ss}(\mathbf{x}, \mathbf{v}_2')} &= \frac{\tilde{\rho}^{ss}(\mathbf{v}_1')}{\tilde{\rho}^{ss}(\mathbf{v}_1)} \\ &= e^{-\frac{\frac{1}{2}m'[(\mathbf{v}_1')^2 - \mathbf{v}_1^2]}{k_B T}} = e^{-\frac{\frac{1}{2}m[\mathbf{v}_2^2 - (\mathbf{v}_2')^2]}{k_B T}}, \end{aligned}$$

followed by

$$\rho^{ss}(\mathbf{x}, \mathbf{v}) = C(\mathbf{x}) e^{-\frac{\frac{1}{2}m\mathbf{v}^2}{k_B T}}. \quad (12)$$

It is just the well-known Maxwell-Boltzmann velocity distribution, which could be rewritten as

$$\frac{k_B T}{m} \nabla_{\mathbf{v}} \log \rho^{ss} = -\mathbf{v}. \quad (13)$$

Therefore, a steady state is at thermal equilibrium if and only if both (8) and (13) are satisfied, i.e.

$$\frac{D}{m} \nabla_{\mathbf{v}} \log \rho^{ss} = \mathbf{F} - \epsilon \mathbf{F} = -\frac{D}{k_B T} \mathbf{v}. \quad (14)$$

Thus at thermal equilibrium, \mathbf{F} could be naturally decomposed into an odd term $-\frac{D}{2k_B T} \mathbf{v}$ and an even term $\frac{\mathbf{F} + \epsilon \mathbf{F}}{2}$. Note that the only odd term is actually the friction force $-\eta \mathbf{v}$.

In thermal equilibrium, $\rho^{ss} = C \exp(-\frac{U(\mathbf{x}) + \frac{1}{2}m\mathbf{v}^2}{k_B T})$, and $\mathbf{F} = -\eta \mathbf{v} - \nabla_{\mathbf{x}} U(\mathbf{x}) + \mathbf{A}(\mathbf{x}, \mathbf{v})$ where \mathbf{A} must be invariant under the inversion of time and satisfies $\nabla_{\mathbf{v}} \cdot (\mathbf{A} \rho^{ss}) = 0$. For example, the Lorentz force $\mathbf{A}(\mathbf{x}, \mathbf{v}) = \mathbf{B} \times \mathbf{v}$ in the electromagnetic field matches the requirement, because both the magnetic force \mathbf{B} and the velocity \mathbf{v} are odd functions under the inversion of time.

Entropy production rates and the equations of entropy balance—Recently, a general definition of entropy production rate through comparison of the probabilities of the original path and its time-reversed path

has been put forward and already applied to stochastic systems with odd and even variables [6, 13]. The entropy production rate is expressed as

$$epr = \int \int \frac{2}{D} \left[\left(\frac{\mathbf{F} - \epsilon \mathbf{F}}{2} \right) - \frac{D}{2m} \nabla_{\mathbf{v}} \log \rho_t \right]^2 \rho_t d\mathbf{x} d\mathbf{v}.$$

The entropy production rate epr is nonnegative. According to the upper equation in (8), $epr = 0$ is equivalent to the time-reversibility of the stochastic system provided that it is in steady state.

The entropy of the stochastic system in the full phase space is defined as $S = -\int \int \rho_t(\mathbf{x}, \mathbf{v}) \log \rho_t(\mathbf{x}, \mathbf{v}) d\mathbf{x} d\mathbf{v}$, hence the entropy balance equation is derived as

$$\begin{aligned} \frac{dS}{dt} &= \int \int [\nabla_{\mathbf{x}} \cdot \mathbf{J}_{\mathbf{x}} + \nabla_{\mathbf{v}} \cdot \mathbf{J}_{\mathbf{v}}] \log \rho_t d\mathbf{x} d\mathbf{v} \\ &= -\int \int [\mathbf{J}_{\mathbf{v}} \cdot \nabla_{\mathbf{v}} \log \rho_t] d\mathbf{x} d\mathbf{v} \\ &= epr - d_e S_1 - d_e S_2, \end{aligned} \quad (15)$$

where

$$d_e S_1 = -\int \int \nabla_{\mathbf{v}} \cdot \left(\frac{\mathbf{F} + \epsilon \mathbf{F}}{2m} \right) \rho_t d\mathbf{x} d\mathbf{v},$$

and

$$\begin{aligned} d_e S_2 &= \int \int \frac{2}{D} \left[\left(\frac{\mathbf{F} - \epsilon \mathbf{F}}{2} \right) - \frac{D}{2m} \nabla_{\mathbf{v}} \log \rho_t \right] \\ &\quad \cdot \left(\frac{\mathbf{F} - \epsilon \mathbf{F}}{2} \right) \rho_t d\mathbf{x} d\mathbf{v}. \end{aligned}$$

On the other hand, according to the second condition of detailed balance (13), one can have another entropy balance equation [18]

$$\frac{dS}{dt} = \widetilde{epr} - \widetilde{d_e S_1} - \widetilde{d_e S_2}, \quad (16)$$

where

$$\widetilde{epr} = \int \int \frac{2}{D} \left[-\eta \mathbf{v} - \frac{D}{2m} \nabla_{\mathbf{v}} \log \rho_t \right]^2 \rho_t d\mathbf{x} d\mathbf{v},$$

$$\widetilde{d_e S_1} = -\int \int \nabla_{\mathbf{v}} \cdot \left(\frac{\mathbf{F} + \eta \mathbf{v}}{m} \right) \rho_t d\mathbf{x} d\mathbf{v},$$

$$\widetilde{d_e S_2} = \frac{1}{k_B T} \int \int \left[\eta \mathbf{v} \rho_t + \frac{D}{2m} \nabla_{\mathbf{v}} \rho_t \right] \cdot \mathbf{v} d\mathbf{x} d\mathbf{v}.$$

This second entropy production rate \widetilde{epr} is nonnegative and $\widetilde{epr} = 0$ is equivalent to the condition (13), which is usually not a consequence of (8). An equilibrium state has to satisfy both of them, i.e. $\widetilde{epr} = 0$ together with $epr = 0$.

Actually, $k_B T \widetilde{d_e S_2}$ is just the heat dissipated into the heat bath [18–20], i.e.

$$\begin{aligned} k_B T \widetilde{d_e S_2} &= -\langle (-\eta \mathbf{v} + \xi(t)) \circ d\mathbf{x} \rangle \\ &= \int \int \left(\eta \mathbf{v} + \frac{D}{2m} \nabla_{\mathbf{v}} \log \rho_t \right) \mathbf{v} \rho_t d\mathbf{x} d\mathbf{v} \\ &= Q(t). \end{aligned} \quad (17)$$

And the work $W(t)$ done by the control force $\mathbf{F}_c = \mathbf{F} + \eta \mathbf{v}$ is

$$\begin{aligned} W(t) &= \langle (\mathbf{F} + \xi(t)) \circ d\mathbf{x} \rangle + Q(t) = \langle \mathbf{v} \circ m d\mathbf{v} \rangle + Q(t) \\ &= \int \int m \mathbf{v} \mathbf{J}_{\mathbf{v}} d\mathbf{x} d\mathbf{v} - Q(t) \\ &= \int \int \mathbf{F}_c \mathbf{v} \rho_t d\mathbf{x} d\mathbf{v}, \end{aligned} \quad (18)$$

which in steady state is equal to $Q(t)$.

In the steady state of the particles in the AFM experiment on nanodevices where $\mathbf{F} = -\eta \mathbf{v} - \alpha \mathbf{v} - \nabla_{\mathbf{x}} U(\mathbf{x})$, we have $\widetilde{epr} = n \frac{\alpha^2}{m(\eta + \alpha)}$, $\widetilde{d_e S_1} = n \frac{\alpha}{m}$, $\widetilde{d_e S_2} = -\frac{n\alpha\eta}{m(\alpha + \eta)}$, where n is the dimension of \mathbf{x} or \mathbf{v} . Recall that $k_B T \cdot \widetilde{d_e S_2} = Q(t)$ is the heat towards the reservoir, therefore, $\widetilde{d_e S_1}$ could be regarded as the increase of the medium entropy due to the irreversible feedback procedure generated by the external agent, and the steady-state entropy production rate $\widetilde{epr} = \widetilde{d_e S_1} + \widetilde{d_e S_2}$ is just the total entropy increase which is positive.

Consistence and inconsistency with overdamped first-order process without inertia— When $\mathbf{F} = -\eta \mathbf{v} + G(\mathbf{x})$ where $G(\mathbf{x})$ is the external force only dependent on the coordinates, these two kinds of entropy balance equations (15) and (16) are equal. In this case, the condition of time-reversibility is equivalent to the steady state to be at equilibrium, which requires

$$\begin{aligned} k_B T \nabla_{\mathbf{v}} \log \rho^{eq} &= -m \mathbf{v}; \\ k_B T \mathbf{v} \cdot \nabla_{\mathbf{x}} \log \rho^{eq} &= -\mathbf{v} \cdot G(\mathbf{x}). \end{aligned}$$

It is easy to prove that it holds if and only if the external force $G(\mathbf{x})$ having a potential and the temperature T is independent of \mathbf{x} .

When the frictional coefficient η is quite large, the stochastic dynamics in the coordinate subspace could be well approximated by the overdamped first-order process, i.e. the corresponding Smoluchowski equation [21, 22]

$$\eta \frac{d\mathbf{X}}{dt} = G(\mathbf{X}) + \xi(t), \quad (19)$$

Furthermore, the distribution in the full phase space $\rho_t(\mathbf{x}, \mathbf{v})$ could be approximated by $q_t(\mathbf{x}, \mathbf{v}) + w_t(\mathbf{x}, \mathbf{v})$ in such a overdamped situation [21], where

$$q_t(\mathbf{x}, \mathbf{v}) = \frac{1}{\left(\sqrt{2\pi \frac{k_B T}{m}} \right)^n} e^{-\frac{\frac{1}{2} m \mathbf{v}^2}{k_B T}} \hat{\rho}_t(\mathbf{x})$$

and

$$\begin{aligned} w_t(\mathbf{x}, \mathbf{v}) &= -\frac{\frac{m \mathbf{v}}{k_B T}}{\eta \left(\sqrt{2\pi \frac{k_B T}{m}} \right)^n} e^{-\frac{\frac{1}{2} m \mathbf{v}^2}{k_B T}} (-G(\mathbf{x}) + k_B T \nabla_{\mathbf{x}}) \hat{\rho}_t(\mathbf{x}). \end{aligned}$$

The $\hat{\rho}_t(\mathbf{x})$ satisfies the Fokker-Planck equation for the Smoluchowski equation (19) [21, 22].

Hence

$$\begin{aligned} &\mathbf{v} + \frac{k_B T}{m} \nabla_{\mathbf{v}} \log \rho_t \\ &\approx \mathbf{v} + \frac{k_B T}{m} \nabla_{\mathbf{v}} \log [q(\mathbf{x}, \mathbf{v}) + w(\mathbf{x}, \mathbf{v})] \\ &= \mathbf{v} + \frac{k_B T}{m} \nabla_{\mathbf{v}} \log q(\mathbf{x}, \mathbf{v}) + \frac{k_B T}{m} \nabla_{\mathbf{v}} \left[\frac{w(\mathbf{x}, \mathbf{v})}{q(\mathbf{x}, \mathbf{v})} \right] \\ &= \frac{k_B T}{m} \nabla_{\mathbf{v}} \left[\frac{w(\mathbf{x}, \mathbf{v})}{q(\mathbf{x}, \mathbf{v})} \right] \\ &= \frac{1}{\eta} [G(\mathbf{x}) - k_B T \nabla_{\mathbf{x}} \log \hat{\rho}_t(\mathbf{x})] \end{aligned} \quad (20)$$

since $w(\mathbf{x}, \mathbf{v}) \ll q(\mathbf{x}, \mathbf{v})$ when η is quite large.

Then, the entropy production rate of the Langevin dynamics

$$\begin{aligned} epr &= \widetilde{epr} = \int \int \frac{2}{D} \left[-\eta \mathbf{v} - \frac{D}{2m} \nabla_{\mathbf{v}} \log \rho_t \right]^2 \rho_t d\mathbf{x} d\mathbf{v} \\ &\approx \int \frac{2}{D} [G(\mathbf{x}) - k_B T \nabla_{\mathbf{x}} \log \hat{\rho}_t(\mathbf{x})]^2 \hat{\rho}_t(\mathbf{x}) d\mathbf{x} \\ &= \hat{epr}, \end{aligned}$$

which is just the entropy production rate for the Smoluchowski equation [7].

Moreover, the entropy of the Langevin dynamics in the full phase space

$$\begin{aligned} S(t) &= \int \int -\rho_t(\mathbf{x}, \mathbf{v}) \log \rho_t(\mathbf{x}, \mathbf{v}) d\mathbf{x} d\mathbf{v} \\ &\approx -\int \int q_t(\mathbf{x}, \mathbf{v}) \log q_t(\mathbf{x}, \mathbf{v}) d\mathbf{x} d\mathbf{v} \\ &= \int -\hat{\rho}_t(\mathbf{x}) \log \hat{\rho}_t(\mathbf{x}) d\mathbf{x} + \frac{n}{2} + \frac{n}{2} \log \frac{2\pi k_B T}{m} \\ &= \hat{S}(t) + \text{constant}, \end{aligned}$$

which followed by $dS(t) = d\hat{S}(t)$.

The condition of time-reversibility associated with the entropy production rate \hat{epr} , is that the field $\frac{G(\mathbf{x})}{k_B T(\mathbf{x})}$ having a potential [7]. Therefore, in the absence of temperature gradient, the established theory of nonequilibrium thermodynamics for the Smoluchowski equation [7–9] is consistent with that of the stochastic dynamics in the full phase space discussed in the present letter.

However, in the presence of temperature gradient, the second-order stochastic process (1) is always time-irreversible, while the Smoluchowski equation (19) still

could be time-reversible, *e.g.* if \mathbf{x} is one-dimensional. It is because the approximation (20) only considers the leading order.

In conclusion, (i) we proposed two conditions of detailed balance for the stochastic system with inertia. (ii) Each condition corresponds to one equation of entropy balance. It clarifies the difference between two previously reported entropy production rates [13, 18]. (iii) For the Langevin equation taking the Smoluchowski equation as its overdamped limit, the two equations of entropy balance are equal. It is consistent with that of the Smoluchowski equation if there is no temperature gradient, but inconsistent in the presence of temperature gradient.

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- [1] Lewis, G.N., Proc. Natl. Acad. Sci. USA, **11** 179-183. (1925)
- [2] Tolman, R. C., The Principles of Statistical Mechanics. Oxford University Press, London, UK. (1938)
- [3] Onsager, L., Phys. Rev. **37**, 405-426. (1931)
- [4] J. Schnakenberg, Rev. Mod. Phys. **48**, 571-585 (1976)
- [5] G. Nicolis and I. Prigogine, *Self-Organization in Nonequilibrium Systems* (Wiley, New York, 1977); T.L. Hill, *Free Energy Transduction in Biology* (Acad. Press, New York, 1977); D.A. Beard and H. Qian, *Chemical Biophysics* (Cambridge Univ. Press, U.K., 2008).
- [6] U. Seifert, Phys. Rev. Lett. **95**, 040602 (2005)
- [7] X.J. Zhang, H. Qian and M. Qian, Phys. Rep. **510**, 1-86 (2012); H. Ge, M. Qian and H. Qian, Phys. Rep. **510**, 87-118 (2012); D.Q. Jiang, M. Qian and M.-P. Qian, *Mathematical Theory of Nonequilibrium Steady States*, LNM vol. 1833, (Springer-Verlag, Berlin, 2004).
- [8] H. Qian, J. Phys. Chem. **110**, 15063-15074 (2006); Annu. Rev. Phys. Chem. **58**, 113-142 (2007); H. Qian and D.A. Beard, Biophys. Chem. **114**, 213-220 (2005).
- [9] H. Ge and H. Qian, Phys. Rev. E **81**, 051133 (2010); M. Esposito and C. van den Broeck, Phys. Rev. Lett. **104**, 090601 (2010); H. Ge, Phys. Rev. E. **80**, 021137 (2009); M. Esposito, U. Harbola and S. Mukamel, Phys. Rev. E. **76**, 031132 (2007).
- [10] H. B. G. Casimir, Rev. Mod. Phys. **17**, 343-350 (1945)
- [11] L. Onsager and S. Machlup, Phys. Rev. **91**, 1505-1512 (1953); S. Machlup and L. Onsager, Phys. Rev. **91**, 1512-1515 (1953)
- [12] H. A. Kramers, Physica, **7**, 284C304 (1941)
- [13] R. E. Spinney and I. J. Ford, Phys. Rev. Lett. **108**, 170603 (2012); Phys. Rev. E **85**, 051113 (2012)
- [14] S. Liang, D. Medich, D. M. Czajkowsky, S. Sheng, J. Yuan and Z. Shao, Ultramicroscopy **84**, 119 (2000)
- [15] Another nontrivial example is when $\rho^{ss} \propto \exp\left(-\frac{\frac{1}{2}m\mathbf{v}^2 g(\mathbf{x}) + U(\mathbf{x})}{k_B T}\right)$. We set $\mathbf{f}_1 = -2\eta\mathbf{v}g(\mathbf{x})$ and \mathbf{f}_2 satisfies

$$\nabla_{\mathbf{v}} \cdot (\mathbf{f}_2 \rho^{ss}) = 2m\mathbf{v} \cdot \left(\frac{m\mathbf{v}^2}{2k_B T} \nabla_{\mathbf{x}} g(\mathbf{x}) + \frac{1}{k_B T} \nabla_{\mathbf{x}} U(\mathbf{x}) \right) \rho^{ss},$$

one solution of which is

$$\mathbf{f}_2 = -m\mathbf{v}^2 \frac{\nabla_{\mathbf{x}} g(\mathbf{x})}{g(\mathbf{x})} - 2k_B T \frac{\nabla_{\mathbf{x}} g(\mathbf{x})}{g(\mathbf{x})^2} - \frac{2\nabla_{\mathbf{x}} U(\mathbf{x})}{g(\mathbf{x})}.$$

The second-order stochastic process (1) with $\mathbf{F} = \frac{\mathbf{f}_1 + \mathbf{f}_2}{2}$ is time-reversible.

- [16] J. C. Maxwell, On the dynamical theory of gases. Phil. Trans. R. Soc. Lond. **157**, 49C88 (1867)
- [17] L. Boltzmann, *Lectures on Gas Theory*, Translated by S.G. Brush (UC Press, Berkeley, 1964).
- [18] K. H. Kim and H. Qian, Phys. Rev. Lett. **93**, 120602 (2005)
- [19] When the temperature is a function of coordinate \mathbf{x} ,

$$\widetilde{d_c S_2} = \int \frac{Q(\mathbf{x}, t)}{k_B T(\mathbf{x})} d\mathbf{x},$$

where $Q(\mathbf{x}, t) = \int (\eta\mathbf{v} + \frac{D}{2m} \nabla_{\mathbf{v}} \log \rho_t) \mathbf{v} \rho_t d\mathbf{v}$ is the local heat dissipation at \mathbf{x} .

- [20] U. Seifert, Eur. Phys. J. E **34**, 26 (2011); K. Sekimoto, *Stochastic Energetics* (Springer-Verlag, Berlin, Heidelberg) (2010)
- [21] Gardiner, C.W., *Handbook of Stochastic Methods for Physics, Chemistry, and the Natural Sciences. 2nd Ed.*, Springer, New York (1985)
- [22] The correct Fokker Planck equation should be in the anti-Ito form. See P. Ao, C. Kwon and H. Qian, Complexity, **12**, 19-27 (2007); G. Volpe, et al., Phys. Rev. Lett. **104**, 170602 (2010)